

## PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
 CP2/5C24  
 Arlington, VA 22202  
 ETATS-UNIS D'AMERIQUE  
 in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 08 June 2001 (08.06.01)	
<b>International application No.</b> PCT/US00/12420	<b>Applicant's or agent's file reference</b> 214-1494WO
<b>International filing date (day/month/year)</b> 03 May 2000 (03.05.00)	<b>Priority date (day/month/year)</b> 03 May 1999 (03.05.99)
<b>Applicant</b> WISDOM, Todd et al	

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

24 November 2000 (24.11.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b>  J. Leitao Telephone No.: (41-22) 338.83.38
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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IS 00/12420

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01F11/46 B01D53/73 B01J10/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01F B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 197711 Derwent Publications Ltd., London, GB; Class E36, AN 1977-18994Y XP002147985 &amp; JP 52 014577 A (NIPPON LIGHT METAL CO), 3 February 1977 (1977-02-03) abstract</p> <p>---</p>	1-6, 12-31
X	<p>PATENT ABSTRACTS OF JAPAN vol. 004, no. 155 (C-029), 29 October 1980 (1980-10-29) &amp; JP 55 099335 A (MITSUI MINING &amp; SMELTING CO LTD), 29 July 1980 (1980-07-29) abstract</p> <p>---</p> <p>-/--</p>	1-6, 12-31

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

21 September 2000

Date of mailing of the international search report

04/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Zalm, W

## INTERNATIONAL SEARCH REPORT

International Application No

P S 00/12420

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	✓ EP 0 706 814 A (MITSUBISHI HEAVY IND LTD) 17 April 1996 (1996-04-17) column 4, line 28 - line 44; claims; figures ---	1-6, 12-31
A	✓ WO 93 19836 A (SMITH JAMES W ;UNIV TORONTO (CA); APOLLO ENVIRONMENTAL SYST CORP ( ) 14 October 1993 (1993-10-14) claim 18; figures ---	1,6
A	✓ EP 0 338 967 A (MITSUBISHI HEAVY IND LTD) 25 October 1989 (1989-10-25) ---	
A	✓ DE 31 04 777 A (HOELTER HEINZ) 2 September 1982 (1982-09-02) -----	

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

P S 00/12420

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 52014577	A	03-02-1977	NONE	
JP 55099335	A	29-07-1980	JP 62022649 B	19-05-1987
EP 0706814	A	17-04-1996	JP 8108035 A	30-04-1996
			CN 1131579 A	25-09-1996
			ES 2140642 T	01-03-2000
			KR 174769 B	18-02-1999
			PL 310910 A	15-04-1996
			US 5665129 A	09-09-1997
WO 9319836	A	14-10-1993	US 5352421 A	04-10-1994
			AU 667093 B	07-03-1996
			AU 3885093 A	08-11-1993
			AU 678936 B	12-06-1997
			AU 5080896 A	27-06-1996
			AU 679407 B	26-06-1997
			AU 5080996 A	27-06-1996
			CA 2133454 A	14-10-1993
			EP 0633810 A	18-01-1995
			FI 944613 A	24-11-1994
			JP 10244122 A	14-09-1998
			JP 7507005 T	03-08-1995
			NO 943651 A	02-12-1994
			US 5413765 A	09-05-1995
			US 5520818 A	28-05-1996
			US 5500135 A	19-03-1996
			US 5585005 A	17-12-1996
			US 5730784 A	24-03-1998
			US 5552061 A	03-09-1996
			US 5527475 A	18-06-1996
			ZA 9302464 A	05-10-1994
EP 0338967	A	25-10-1989	JP 1258733 A	16-10-1989
			JP 2505525 B	12-06-1996
			AU 3242989 A	12-10-1989
			BR 8901652 A	21-11-1989
			DE 68916583 D	11-08-1994
			DE 68916583 T	27-10-1994
			DK 167789 A	09-10-1989
			ES 2056245 T	01-10-1994
			US 4955586 A	11-09-1990
DE 3104777	A	02-09-1982	NONE	

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
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AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
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EE	Estonia	LR	Liberia	SG	Singapore		

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>214-14947W0</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/US 00/12420</b>	International filing date (day/month/year) <b>03/05/2000</b>	(Earliest) Priority Date (day/month/year) <b>03/05/1999</b>
Applicant <b>BAKER HUGHES INCORPORATED et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of Invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1

☐ None of the figures.

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 18 OCT 2001

WIPO

PCT

Applicant's or agent's file reference 214-14947WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/12420	International filing date (day/month/year) 03 MAY 2000	Priority date (day/month/year) 03 MAY 1999
International Patent Classification (IPC) or national classification and IPC IPC(7): B01F 3/04 and US Cl.: 422/231, 168, 224, 225, 226		
Applicant BAKER HUGHES INCORPORATED		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 6 sheets.  
☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
These annexes consist of a total of 0 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability, citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 03 MAY 2001	Date of completion of this report 08 SEPTEMBER 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer Rick Varcoe DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/12420

## I. Basis of the report

1. With regard to the elements of the international application:\*

☒ the international application as originally filed

☒ the description:

pages 1-19, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of \_\_\_\_\_

☒ the claims:

pages 20-24, as originally filed  
pages NONE, as amended (together with any statement) under Article 19  
pages NONE, filed with the demand  
pages NONE, filed with the letter of \_\_\_\_\_

☒ the drawings:

pages 1-4, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of \_\_\_\_\_

☒ the sequence listing part of the description:

pages NONE, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of \_\_\_\_\_

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.  
These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in printed form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

- ☒ the description, pages NONE  
☒ the claims, Nos. NONE  
☒ the drawings, sheets/fig NONE

5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\*Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/12420

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. statement

Novelty (N)

Claims 1-31

YES

Claims NONE

NO

Inventive Step (IS)

Claims NONE

YES

Claims 1-31

NO

Industrial Applicability (IA)

Claims 1-31

YES

Claims NONE

NO

### 2. citations and explanations (Rule 70.7)

Claims 1-20 and 22-31 lack an inventive step under PCT Article 35(3) as being obvious over Okazoe et al., EP 0706814 A1 in view of Smith et al., US 5,413,765.

With regard to claim 1, Okazoe discloses an oxidative reactor to support formation and precipitation of calcium sulfate from calcium sulfite, the reactor comprising: a tank (Figure 1 (21) having walls and a bottom, for holding an aqueous slurry of calcium sulfite, an inlet in the tank (Figure 1) for delivery of the aqueous slurry from a source, a fine (column 4 lines 40-44) bubble generator (Figure 1 (30,31,32,22)), a mixer (Figure 1 (30,31,32,22)) in the tank to distribute the bubbles into the aqueous slurry and to maintain the circulation of the aqueous slurry and bubbles in the tank.

Okazoe fails expressly to disclose a flow diverter in the tank to reduce rotation of the aqueous solution in the tank.

Smith discloses a flow diverter in the tank to reduce rotation of the aqueous solution in the tank (Figure 2 (34)).

At the time of the invention it would have been obvious to one skilled in the art to combine the flow diverter of Smith with the apparatus of Okazoe. The motivation would have been to effect rapid mass transfer between gaseous and liquid phases (Smith column 3 lines 10-12).

With regard to claim 2, Okazoe discloses use of air in the reactor line (Okazoe column 4 line 12).

With regard to claim 3, the temperature of the air is an intended use and not a structural element of the apparatus.

With regard to claim 4, Okazoe discloses a rotor rotatable in the tank and constituting at least part of the fine bubble generator (Figure 1 (30,31,32,22)). While no washer is recited in this or the claims from which it depends, the rotor and flow diverter of Okazoe function to wash the rotor.

With regard to claim 5, Okazoe's rotor constitutes a mixer (Figure 1 (30,31,32,22)).

(Continued on Supplemental Sheet.)

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/12420

## Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Sheet 10

Continuation of: Boxes I - VIII

### V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):

With regard to claim 6, Okazoe's rotor has an interior cavity (Figure 1 (31)) and constitutes at least part of the fine bubble generator. While Okazoe does not expressly mention use of a gas permeable material, it would have been obvious to one skilled in the art to use gas permeable material to transfer gas. The motivation would have been to maintain structural integrity while at the same time allowing gas to pass through the apparatus.

With regard to claim 7, Smith discloses a stator assembly (Figure 2 (34)) around the rotor defining flow paths for the aqueous slurry and constituting at least a part of the mixer. At the time of the invention it would have been obvious to one skilled in the art to combine the stator assembly of Smith with the apparatus of Okazoe. The motivation would have been to effect rapid mass transfer between gaseous and liquid phases (Smith column 3 lines 10-12).

With regard to claim 8, Okazoe discloses a standpipe mounted above the fine bubble generator (Figure 1 (31)).

With regard to claim 9, Smith's flow diverter and mixer (or Okazoe's mixer) taken together function the same was as the apparatus of the present claim. While neither Okazoe nor Smith expressly discloses the fact that their apparatus washes solids from the fine bubble generator, since the apparatus is the same as that in the prior art, that function is also present in the prior art. Identifying functions that were present in the prior art does not make those functions nonobvious.

With regard to claim 10, Smith discloses a draft tube (Figure 5 (110) column 18 line 38). At the time of the invention it would have been obvious to include a draft tube in the apparatus of Okazoe. The motivation would have been to guide the liquid into the region of the impeller (Smith column 18 lines 38-41).

With regard to claim 11, Smith discloses a false floor (Figure 1) below the mixer. At the time of the invention it would have been obvious to place a false floor below the draft tube in the modified apparatus of Okazoe. The motivation would have been to further control the flow of the slurry in the system.

With regard to claim 12, Okazoe discloses an inlet and outlet in the tank positioned close to the bottom of the tank.

With regard to claim 13, Okazoe discloses a reactor tank with a top at least partially vented to the atmosphere. The terms "adiabatic cooling" and "releases gas and heat" are contradictory since "adiabatic" means neither releases nor acquires heat from outside the system.

With regard to claim 14, since the size of the particles is not a structural feature of the apparatus, the rejection of claim 1 applies.

With regard to claim 15, Okazoe discloses an oxidative reactor to support formation and precipitation of calcium sulfate from calcium sulfite, the reactor comprising: a tank (Figure 1 (21) having walls and a bottom, for holding an aqueous slurry of calcium sulfite, an inlet in the tank (Figure 1) for delivery of the aqueous slurry from a source, a fine (column 4 lines 40-44) bubble generator (Figure 1 (30,31,32,22)), a mixer (Figure 1 (30,31,32,22)) in the tank to distribute the bubbles into the aqueous slurry and to maintain the circulation of the aqueous slurry and bubbles in the tank.

Okazoe fails expressly to disclose a flow diverter in the tank to reduce rotation of the aqueous solution in the tank.

Smith discloses a flow diverter in the tank to reduce rotation of the aqueous solution in the tank (Figure 2 (34)).

At the time of the invention it would have been obvious to one skilled in the art to combine the flow diverter of Smith with the apparatus of Okazoe. The motivation would have been to effect rapid mass transfer between gaseous and liquid phases (Smith column 3 lines 10-12).

With regard to claim 16, Okazoe discloses a scrubber (Figure 1) constituting a source for the aqueous solution.

With regard to claim 17, Smith's flow diverter and mixer (or Okazoe's mixer) taken together function the same was as the apparatus of the present claim. While neither Okazoe nor Smith expressly discloses the fact that their apparatus washes solids from the fine bubble generator, since the apparatus is the same as that in the prior art, that function is also present in the prior art. Identifying functions that were present in the prior art does not make those functions nonobvious.

With regard to claim 18, the temperature of the air is an intended use and not a structural element of the apparatus.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/12420

**Supplemental Box**  
(To be used when the space in any of the preceding boxes is not sufficient)

Sheet 11

Continuation of: Boxes I - VIII

With regard to claim 19, Okazoe discloses an aqueous solution of calcium sulfite. This claim states that the solution is a slurry. Since a slurry contains particles and a solution does not, this seems to be contradictory language.

With regard to claim 20, Okazoe discloses a dewatering device (Figure 1).

With regard to claims 22 and 23, Okazoe discloses a second dewatering device constituting a vacuum filter (Figure 1).

With regard to claim 24, Okazoe discloses a method for formation of oxidized salts from an aqueous solution of salts comprising:

providing a tank (Figure 1 (21) having an inlet,

introducing an aqueous solution containing a reduced salt to the tank (column 1 lines 34-47),

delivering a flow of fine bubbles of an oxygen-containing gas to the tank via a fine bubble generator, (column 1 lines

34-47),

mixing the bubbles and the solution to distribute the bubbles into the solution (column 1 lines 34-47),

circulating the aqueous solution and bubbles in the tank (column 1 lines 34-47).

Okazoe does not expressly disclose reducing the rotation of the aqueous solution in the tank. Smith discloses reducing the rotation of the aqueous solution in the tank. Smith's shroud (Figure 2 (34) that surrounds the impeller reduces the rotation of the solution in the tank. At the time of the invention it would have been obvious to one skilled in the art to add the shroud of Smith to the apparatus used in the process of Okazoe. The motivation would have been to further disperse the bubbles in the solution and effect mass transfer and rapid reaction (Abstract).

Okazoe discloses oxidizing the salt to its oxidized form (column 1 lines 34-47). Okazoe discloses circulating the solution and bubbles in the tank (column 1 lines 34-47).

With regard to claim 25, Okazoe discloses providing air as the gas (column 1 line 45).

With regard to claim 26, lacking disclosure to the contrary, the air supplied by Okazoe can be considered to be at ambient temperature.

With regard to claim 27, Okazoe discloses adjusting the pH (column 6 lines 1-8). The particular value chosen is result-effective and within the ability of one of ordinary skill in the art.

With regard to claim 28, Okazoe discloses aqueous solution provided from a scrubber (Figure 1).

With regard to claim 29, Okazoe discloses desulfurizing flue gas in the scrubber to form a reduced salt comprising a sulfite (column 1 lines 34-47).

With regard to claim 30, while the modified process of Okazoe does not expressly contain a description of cleaning solids from the bubble generator, since the prior art apparatus has the same features as that of the present invention, the same cleaning activity described for the present invention also takes place with the apparatus of the prior art.

With regard to claim 31, Okazoe discloses dewatering the oxidized salt (Figure 1).

Claim 21 lacks an inventive step under PCT Article 33(3) as being obvious over Okazoe et al., EP 0706814 A1 and Smith et al., US 5,413,765 as applied to claims 1-20 and 21-31 above, and further in view of Kuroda et al., US 5,648,048.

With regard to claim 21, the modified apparatus of Okazoe discloses essentially the same apparatus as the present claim but fails expressly to include a hydrocyclone. Kuroda (column 15 lines 1-15) discloses use of a hydrocyclone. Okazoe and Kuroda are analogous in that both deal with wet flue gas desulfurization apparatus. At the time of the invention it would have been obvious to one skilled in the art to use a hydrocyclone in the modified apparatus of Okazoe. The motivation would have been to thicken the gypsum in the slurry (column 15 line 8).

## NEW CITATIONS

US 5,413,765 (Smith et al.) 09 MAY 1995, see Figures 1, 2 and 4.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/12420

**Supplemental Box**

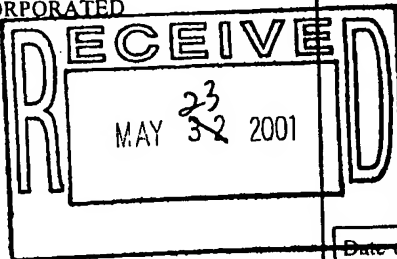
(To be used when the space in any of the preceding boxes is not sufficient)

Sheet 12

Continuation of: Boxes I - VIII

US 5,648,048 (Kuroda et al.) 15 JULY 1997, see column 15 lines 1-15.

## PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITYTo: ALBERT J. RIDDLE  
BAKER HUGHES INCORPORATED  
3900 ESSEX LANE  
SUITE 1200  
HOUSTON TX 77027

PCT

WRITTEN OPINION

(PCT Rule 66)

5/30/01  
JCP

Re: B19-061

Date of Mailing  
(day/month/year)

17 MAY 2001

Applicant's or agent's file reference

214-14947WO

REPLY DUE

within TWO months  
from the above date of mailing

International application No.

PCT/US00/12420

International filing date (day/month/year)

03 MAY 2000

Priority date (day/month/year)

03 MAY 1999

International Patent Classification (IPC) or both national classification and IPC  
IPC(7): B01F 3/04 and US Cl.: 422/231, 168, 224, 225, 226

Applicant

BAKER HUGHES INCORPORATED

1. This written opinion is the first (first, etc.) drawn by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. ~~The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).~~

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4. For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis. For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 03 SEPTEMBER 2001Name and mailing address of the IPEA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

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PARALEGAL SPECIALIST

7-17-01

## WRITTEN OPINION

International application No.

PCT/US00/12420

## I. Basis of the opinion

## 1. With regard to the elements of the international application:\*

☒ the international application as originally filed☒ the description:

pages 1-19, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of

☒ the claims:

pages 20-24, as originally filed  
pages NONE, as amended (together with any statement) under Article 19  
pages NONE, filed with the demand  
pages NONE, filed with the letter of

☒ the drawings:

pages 1-4, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of

☒ the sequence listing part of the description:

pages NONE, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.  
These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

## 3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the written opinion was drawn on the basis of the sequence listing:

- ☐ contained in the international application in printed form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

- ☒ the description, pages NONE  
☒ the claims, Nos. NONE  
☒ the drawings, sheets/fig NONE

5. ☐ This opinion has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".

## WRITTEN OPINION

International application No.

PCT/US00/12420

**V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. statement**

Novelty (N)	Claims <u>1-31</u>	YES
	Claims <u>NONE</u>	NO
Inventive Step (IS)	Claims <u>NONE</u>	YES
	Claims <u>1-31</u>	NO
Industrial Applicability (IA)	Claims <u>1-31</u>	YES
	Claims <u>NONE</u>	NO

**2. citations and explanations**

Claims 1-20 and 22-31 lack an inventive step under PCT Article 33(3) as being obvious over Okazoe et al., EP 0706814 A1 in view of Smith et al., US 5,413,765.

With regard to claim 1, Okazoe discloses an oxidative reactor to support formation and precipitation of calcium sulfate from calcium sulfite, the reactor comprising; a tank (Figure 1 (21) having walls and a bottom, for holding an aqueous slurry of calcium sulfite, an inlet in the tank (Figure 1) for delivery of the aqueous slurry from a source, a fine (column 4 lines 40-44) bubble generator (Figure 1 (30,31,32,22)), a mixer (Figure 1 (30,31,32,22)) in the tank to distribute the bubbles into the aqueous slurry and to maintain the circulation of the aqueous slurry and bubbles in the tank.

Okazoe fails expressly to disclose a flow diverter in the tank to reduce rotation of the aqueous solution in the tank.

Smith discloses a flow diverter in the tank to reduce rotation of the aqueous solution in the tank (Figure 2 (34)).

At the time of the invention it would have been obvious to one skilled in the art to combine the flow diverter of Smith with the apparatus of Okazoe. The motivation would have been to effect rapid mass transfer between gaseous and liquid phases (Smith column 3 lines 10-12).

With regard to claim 2, Okazoe discloses use of air in the reactor line (Okazoe column 4 line 12).

With regard to claim 3, the temperature of the air is an intended use and not a structural element of the apparatus.

With regard to claim 4, Okazoe discloses a rotor rotatable in the tank and constituting at least part of the fine bubble generator (Figure 1 (30,31,32,22)). While no washer is recited in this or the claims from which it depends, the rotor and flow diverter of Okazoe function to wash the rotor.

With regard to claim 5, Okazoe's rotor constitutes a mixer (Figure 1 (30,31,32,22)).

(Continued on Supplemental Sheet.)

## WRITTEN OPINION

International application No.

PCT/US00/12420

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 1-14 and 19 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claims are indefinite for the following reason(s): in line 10 of claim 1, "said aqueous solution" lacks clear antecedent basis. Solution s and slurries are different.

Claim 13 recites releasing heat from the reactor to the atmosphere and facilitating adiabatic cooling. "Adiabatic" refers to processes where no heat is added or removed from the vessel. There is thus a logical conflict presented here.

Claim 19 recites a solution that is a slurry. Solutions and slurries are different. A slurry has particles, where a solution does not. A slurry can be prepared from a solution, but it is not a solution itself.



## WRITTEN OPINION

International application No.

PCT/US00/12420

## Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Sheet 10

Continuation of: Boxes I - VIII

## TIME LIMIT:

The time limit set for response to a Written Opinion may not be extended. 37 CFR 1.484(d). Any response received after the expiration of the time limit set in the Written Opinion will not be considered in preparing the International Preliminary Examination Report.

## V. 2. REASONED STATEMENT: CITATIONS AND EXPLANATIONS (Continued):

With regard to claim 6, Okazoe's rotor has an interior cavity (Figure 1 (31)) and constitutes at least part of the fine bubble generator. While Okazoe does not expressly mention use of a gas permeable material, it would have been obvious to one skilled in the art to use gas permeable material to transfer gas. The motivation would have been to maintain structural integrity while at the same time allowing gas to pass through the apparatus.

With regard to claim 7, Smith discloses a stator assembly (Figure 2 (34)) around the rotor defining flow paths for the aqueous slurry and constituting at least a part of the mixer. At the time of the invention it would have been obvious to one skilled in the art to combine the stator assembly of Smith with the apparatus of Okazoe. The motivation would have been to effect rapid mass transfer between gaseous and liquid phases (Smith column 3 lines 10-12).

With regard to claim 8, Okazoe discloses a standpipe mounted above the fine bubble generator (Figure 1 (31)).

With regard to claim 9, Smith's flow diverter and mixer (or Okazoe's mixer) taken together function the same as the apparatus of the present claim. While neither Okazoe nor Smith expressly discloses the fact that their apparatus washes solids from the fine bubble generator, since the apparatus is the same as that in the prior art, that function is also present in the prior art. Identifying functions that were present in the prior art does not make those functions nonobvious.

With regard to claim 10, Smith discloses a draft tube (Figure 5 (110) column 18 line 38). At the time of the invention it would have been obvious to include a draft tube in the apparatus of Okazoe. The motivation would have been to guide the liquid into the region of the impeller (Smith column 18 lines 38-41).

With regard to claim 11, Smith discloses a false floor (Figure 1) below the mixer. At the time of the invention it would have been obvious to place a false floor below the draft tube in the modified apparatus of Okazoe. The motivation would have been to further control the flow of the slurry in the system.

With regard to claim 12, Okazoe discloses an inlet and inlet in the tank positioned close to the bottom of the tank.

With regard to claim 13, Okazoe discloses a reactor tank with a top at least partially vented to the atmosphere. The terms "adiabatic cooling" and "releases gas and heat" are contradictory since "adiabatic" means neither releases nor acquires heat from outside the system.

With regard to claim 14, since the size of the particles is not a structural feature of the apparatus, the rejection of claim 1 applies.

With regard to claim 15, Okazoe discloses an oxidative reactor to support formation and precipitation of calcium sulfate from calcium sulfite, the reactor comprising; a tank (Figure 1 (21) having walls and a bottom, for holding an aqueous slurry of calcium sulfite, an inlet in the tank (Figure 1) for delivery of the aqueous slurry from a source, a fine (column 4 lines 40-44) bubble generator (Figure 1 (30,31,32,22)), a mixer (Figure 1 (30,31,32,22)) in the tank to distribute the bubbles into the aqueous slurry and to maintain the circulation of the aqueous slurry and bubbles in the tank.

Okazoe fails expressly to disclose a flow diverter in the tank to reduce rotation of the aqueous solution in the tank. Smith discloses a flow diverter in the tank to reduce rotation of the aqueous solution in the tank (Figure 2 (34)).

At the time of the invention it would have been obvious to one skilled in the art to combine the flow diverter of Smith with the apparatus of Okazoe. The motivation would have been to effect rapid mass transfer between gaseous and liquid phases (Smith column 3 lines 10-12).

With regard to claim 16, Okazoe discloses a scrubber (Figure 1) constituting a source for the aqueous solution.

## WRITTEN OPINION

International application No.

PCT/US00/12420

## Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Sheet 11

Continuation of: Boxes I - VIII

With regard to claim 17, Smith's flow diverter and mixer (or Okazoe's mixer) taken together function the same as the apparatus of the present claim. While neither Okazoe nor Smith expressly discloses the fact that their apparatus washes solids from the fine bubble generator, since the apparatus is the same as that in the prior art, that function is also present in the prior art. Identifying functions that were present in the prior art does not make those functions nonobvious.

With regard to claim 18, the temperature of the air is an intended use and not a structural element of the apparatus.

With regard to claim 19, Okazoe discloses an aqueous solution of calcium sulfite. This claim states that the solution is a slurry. Since a slurry contains particles and a solution does not, this seems to be contradictory language.

With regard to claim 20, Okazoe discloses a dewatering device (Figure 1).

With regard to claims 22 and 23, Okazoe discloses a second dewatering device constituting a vacuum filter (Figure 1).

With regard to claim 24, Okazoe discloses a method for formation of oxidized salts from an aqueous solution of salts comprising:

providing a tank (Figure 1 (21) having an inlet,  
introducing an aqueous solution containing a reduced salt to the tank (column 1 lines 34-47),  
delivering a flow of fine bubbles of an oxygen-containing gas to the tank via a fine bubble generator, (column 1 lines

34-47),  
mixing the bubbles and the solution to distribute the bubbles into the solution (column 1 lines 34-47),

circulating the aqueous solution and bubbles in the tank (column 1 lines 34-47).

Okazoe does not expressly disclose reducing the rotation of the aqueous solution in the tank. Smith discloses reducing the rotation of the aqueous solution in the tank. Smith's shroud (Figure 2 (34) that surrounds the impeller reduces the rotation of the solution in the tank. At the time of the invention it would have been obvious to one skilled in the art to add the shroud of Smith to the apparatus used in the process of Okazoe. The motivation would have been to further disperse the bubbles in the solution and effect mass transfer and rapid reaction (Abstract).

Okazoe discloses oxidizing the salt to its oxidized form (column 1 lines 34-47). Okazoe discloses circulating the solution and bubbles in the tank (column 1 lines 34-47).

With regard to claim 25, Okazoe discloses providing air as the gas (column 1 line 45).

With regard to claim 26, lacking disclosure to the contrary, the air supplied by Okazoe can be considered to be at ambient temperature.

With regard to claim 27, Okazoe discloses adjusting the pH (column 6 lines 1-8). The particular value chosen is result-effective and within the ability of one of ordinary skill in the art.

With regard to claim 28, Okazoe discloses aqueous solution provided from a scrubber (Figure 1).

With regard to claim 29, Okazoe discloses desulfurizing flue gas in the scrubber to form a reduced salt comprising a sulfite (column 1 lines 34-47).

With regard to claim 30, while the modified process of Okazoe does not expressly contain a description of cleaning solids from the bubble generator, since the prior art apparatus has the same features as that of the present invention, the same cleaning activity described for the present invention also takes place with the apparatus of the prior art.

With regard to claim 31, Okazoe discloses dewatering the oxidized salt (Figure 1).

Claim 21 lacks an inventive step under PCT Article 33(3) as being obvious over Okazoe et al., EP 0706814 A1 and Smith et al., US 5,413,765 as applied to claims 1-20 and 21-31 above, and further in view of Kuroda et al., US 5,648,048.

With regard to claim 21, the modified apparatus of Okazoe discloses essentially the same apparatus as the present claim but fails expressly to include a hydrocyclone. Kuroda (column 15 lines 1-15) discloses use of a hydrocyclone. Okazoe and Kuroda are analogous in that both deal with wet flue gas desulfurization apparatus. At the time of the invention it would have been obvious to one skilled in the art to use a

## WRITTEN OPINION

International application No.

PCT/US00/12420

**Supplemental Box**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 12

hydrocyclone in the modified apparatus of Okazoe. The motivation would have been to thicken the gypsum in the slurry (column 15 line 8).

## ----- NEW CITATIONS -----

US 5,413,765 (Smith et al.) 09 MAY 1995, see Figures 1, 2 and 4.

US 5,648,048 (Kuroda et al.) 15 JULY 1997, see column 15 lines 1-15.

## OXIDATIVE REACTOR FOR OXIDATION OF SALTS

### CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/132,273, filed May 3, 1999, U.S. Provisional Application No. 60/149,557, filed August 18, 1999, and Provisional Application No. 60/165,956, filed November 17, 1999.

### BACKGROUND OF THE INVENTION

This invention relates to an oxidative reactor and method for forming oxidized salts from reduced salts. More particularly, this invention relates to an oxidative reactor providing high rates of oxygen transfer for oxidizing salts, such as calcium, sodium, magnesium and/or ammonium sulfite and iron salts, to their oxidized forms, and methods of using that reactor.

As power utilities and manufacturing plants increase the use of pollution control equipment to meet the emission standards of the Clean Air Act, the volume of flue gas desulfurization by-products is increasing. Those by-products must be disposed of according to the requirements of the Resource Conservation and Recovery Act (RCRA). RCRA requires that waste products are disposed of in ponds or landfills according to certain specified standards. The disposal of such by-products in those landfills and ponds is becoming more difficult because the volume of wastes continues to increase. Furthermore, as liner and groundwater monitoring requirements become more stringent, the cost of disposing of those by-products as wastes is rising rapidly. Consequently, many power utilities and manufacturing plants are seeking alternate routes for the disposal of flue gas desulfurization by-products. In particular, those plants are seeking efficient, cost-effective equipment and methods for converting such by-products into useful recycled materials. Such equipment and methods can not only help to avoid the regulatory requirements of RCRA, but the sale of such recycled materials can partially offset the costs of purchasing and operating pollution control equipment.

Most FGD processes utilize a basic absorbent to remove sulfur by-products from combustion. The most common of these FGD systems use alkaline earth metal compounds, calcium, magnesium, and sodium, or ammonia, as the absorbents. These absorbents form the corresponding sulfite salt in the FGD process. Most of these FGD processes eventually produce calcium sulfite or calcium sulfate as the final waste product. This waste product may also contain some of sodium or magnesium sulfite or sulfate salts. To a lesser extent ammonium and magnesium sulfite salts are produced individually. Calcium sulfite is not readily reusable in manufacturing processes, however, so it is disposed of in landfills or oxidized, either *in-situ* or *ex-situ*, to calcium sulfate. The other sulfite salts, such as sodium, ammonium and/or magnesium sulfites can also be oxidized. Such sulfite salts also present disposal problems. However, calcium, magnesium, and ammonium sulfate salts all have some commercial value associated with them.

For many power utilities and manufacturing plants, adding pollution control equipment to effect the conversion of flue gas desulfurization by-products into useful products requires some modification of the existing pollution control process. Such modification of the scrubber systems typically includes the addition of equipment to oxidize sulfites to sulfates (for example, oxidizing calcium sulfite to calcium sulfate (gypsum)), *in-situ* or *ex-situ*, followed by the precipitation and/or dewatering of the sulfate salt. The *ex-situ* equipment currently in use is a tower with coarse air bubble diffusers. Oxidizing towers are typically inefficient because they have large water columns. To generate sufficient air pressure and volume to form bubbles to oxygenate the water column, large air compressors are required. Such large compressors generate significant heat, which is transferred to the water column through the diffusers. As the water temperature increases, the solubility of oxygen decreases, thereby decreasing the efficiency of the oxidation process. The oxidation of sulfite salts to sulfate salts in these towers also heats the water column, which further decreases the solubility of oxygen. To counteract these heating effects, air/water heat exchangers or humidifiers are used to cool the compressed air

prior to injection into the tower. The requirement for heat exchangers or humidifiers markedly increases the operating costs of such equipment.

A related disadvantage of current oxidation tower designs is that the diffusers are prone to clogging as scale forms around the apertures in the diffusers. In particular, diffusers have small apertures can be quickly clogged and rendered inoperable. To overcome such problems, diffusers are designed with large apertures. While large apertures are less prone to clogging, they have the resultant disadvantage of producing the above-noted large gas bubbles with low surface to volume ratios. Such large bubbles inefficiently transfer oxygen to the surrounding liquid. To overcome that problem, the volume of air bubbling through the tower must be increased, which requires larger compressors. A further problem with such tower designs is that the hydrostatic head pressure markedly changes as the bubbles rise in the column. Consequently, as the bubbles rise, they expand and their surface area to volume ratio decreases, as does the rate of oxygen transfer to the surrounding liquid. The oxidation rate of sulfite to sulfate also decreases.

In summary, current tower designs are energy-intensive because they require large air volumes to provide sufficient aeration to oxidize sulfite salts to their sulfate forms. The coarse air bubble diffusers used in those designs fail to efficiently oxidize sulfites because they generate large bubbles with small surface area to volume ratios, and thereby effect low rates of oxygen transfer. Furthermore, those designs, when modified to produce small bubbles, are subject to clogging scale buildup which requires frequent maintenance. To overcome the deficiencies of current tower designs, a reactor is needed that provides a high rate of oxidation of sulfite salts to their sulfate forms while preventing the formation of scale on the aerators. Such a reactor should provide a high rate of oxygen transfer via fine bubbles of an oxygen-containing gas that have a large surface area to volume ratio to enhance the oxygen-transfer to the surrounding liquid, yet remain free of scale buildup that interferes with the dispensing of fine bubbles.

## SUMMARY OF THE INVENTIONS

In accordance with the present inventions, an oxidative reactor with a fine bubble generator provides a high rate of oxygen transfer to oxidize reduced salts to their oxidized forms. The bubble generator introduces a stream of fine bubbles of an oxygen-containing gas into a solution containing one or more reduced salts. Such a solution can be, for example, an aqueous slurry of a reduced salt (e.g. calcium sulfite), a sulfite salt dissolved in an aqueous solution (e.g. ammonium sulfite or iron sulfate), and/or a dissolved salt in equilibrium with a slurry. A mixer distributes those bubbles into the solution to effect a high rate of oxygen transfer to that solution. As the reduced salt reacts with the oxygen, it is oxidized. Advantageously, a washer can optionally prevent the deposition of solids, such as sulfate salts and scale, on the fine bubble generator and aids in removing such solids from that generator. The oxidative reactor can be operated in either continuous or batch modes. A system of one or more oxidative reactors, connected in series and/or in parallel, can be provided to facilitate the oxidation of reduced salts and/or to allow individual reactors to be taken off-line for maintenance and/or repair.

In accordance with another aspect, a method is provided for rapidly forming oxidized salts from their reduced forms. A flow of fine bubbles of an oxygen-containing gas, produced by a fine bubble generator, is delivered to an aqueous solution containing one or more reduced salts. Mixing the bubbles into the aqueous solution provides a high rate of oxygen transfer to that solution to support a high rate of oxidation of reduced salt to its oxidized form. Advantageously, any solids that accumulate on the fine bubble generator during sulfate formation are optionally cleaned from that generator so that the generator remains substantially free of such solids.

Among the objects disclosed herein is that the oxidative reactor has a fine bubble generator that supports a high rate of transfer of an oxygen-containing gas to a solution containing a reduced salt.

Among the further objects disclosed is that the oxidative reactor optionally includes a washer that prevents the deposition of solids on the fine bubble generator and aids in removing such solids that form on the generator.

Among the further objects disclosed is a system of oxidative reactors that can be operated in series or in parallel for the continuous or batch processing of reduced salts, to allow individual reactors to be taken off-line for maintenance or repair, and to allow regulation of the system according to the amount of reduced salt being processed.

Among the further objects disclosed is a method of oxidizing sulfite salts to sulfates via high rates of oxygen transfer to an aqueous solution containing suspended sulfite salts.

Additional objects and advantages will become apparent to those skilled in the art upon examination of the following description, figures and claims.

#### DESCRIPTION OF THE DRAWINGS

Figure 1 is a side view of one embodiment of the reactor with portions of the tank wall cut away;

Figure 2 is a side view of an embodiment that includes a gas transfer mechanism;

Figure 3 is a side view of a second embodiment of the reactor with portions of the tank wall cut away;

Figure 4 is a side view of a third embodiment of the reactor;

Figures 5a and 5b are flow diagrams of a series of reactors; and

Figure 6 is a side view of an embodiment of a reactor with portions of the sidewall cut away.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to Figure 1, there is generally indicated a single cell embodiment of a reactor for oxidizing reduced salt to their oxidized forms. The reactor 10 includes a liquid-holding tank 15. As illustrated, the tank 15 has a generally



rectangular or circular configuration and is defined by sidewalls 12 and bottom wall 14. Other configurations of tank 15 are also possible. Preferably, the top of tank 15 is open to accommodate high rates of aeration and to cool the reactor by allowing liquid to evaporate and heat otherwise to dissipate.

Tank 15 is constructed of any suitable material for containing aqueous reduced salt and their oxidized forms. For example, tank 15 is constructed from a chemically-resistant material, such as stainless steel or fiberglass, that is resistant to the corrosive effects of chlorine, sulfite salts, sulfate salts and/or acids. Tank 15 can also be constructed so that it has a chemically-resistant coating, such as an elastomer-covered mild steel. Other suitable chemically-resistant coatings include rubber, polyurethane, TEFLON<sup>®</sup> (polytetrafluoroethylene) or other materials that resist the corrosive effects of chlorine, sulfite salts, sulfate salts and/or acids. Other designs of tank 15 are possible, such as, for example, a trench with a concrete base and or sidewalls.

Tank 15 includes one or more apertures 20 for the delivery of the reduced salts to tank 15 and for the discharge of oxidized salts from tank 15. Alternatively, the reduced salt feed may be delivered through the top of the open tank 15 via a pipe. In one embodiment as shown, tank 15 has more than one aperture 20, including at least one inlet 25 and at least one outlet 30. Inlet 25 provides for the delivery of reduced salts to tank 15, and outlet 30 provides for the discharge of oxidized salts from tank 15. Each aperture 20, including an inlet 25 or outlet 30, can be positioned at any suitable location on tank 15. For example, Figure 1 depicts an inlet 25 located at an elevated position relative to outlet 30. The inlet 25 can also be structured to introduce reduced salt near the top or bottom of tank 15. Preferably, at least one inlet 25 and at least one outlet 30 are located at substantially the same elevation above the tank bottom and in a lower portion of tank 15, such as in the lower half of the tank. As will be appreciated by those skilled in the art, other means for delivering reduced salts into, and discharging oxidized salts from, tank 15 are within the scope of the invention. In the illustrated embodiment, reactor 10 has a false floor 40. Such a false floor 40 can be perforated to facilitate the flow of

aqueous solution 35 in tank 15. In other embodiments, the reactor 10 omits that false floor 40.

Tank 15 can contain a solution of one or more reduced salts, such as, for example, alkali or alkaline sulfite salts (*e.g.*, sodium or calcium), magnesium and/or ammonium sulfite salts, and iron sulfate. Such salts can be dissolved and/or suspended in the aqueous solution. For example, in one embodiment, tank 15 can hold a quantity of an aqueous slurry 35 of suspended calcium sulfite solids in equilibrium with dissolved calcium sulfite in solution. The calcium sulfite is preferably about 5 to about 25 % (w/v) suspended solids, although greater and lesser concentrations are within the scope of the invention. More preferably, the calcium sulfite slurry is about 15% to 25% (w/v) suspended solids. The slurry 35 can further include a supersaturated slurry. The concentration of calcium sulfite in the slurry 35 in tank 15 can be adjusted by the introduction of water, aqueous calcium sulfite, another aqueous medium, or solid calcium sulfite. The pH of the calcium sulfite slurry 35 in tank 15 is preferably acidic, within the range of about 3 to about 7. In a more preferred embodiment, the pH is between about 4.5 to about 5.5. The pH can be adjusted with any suitable acid, including, for example, sulfuric acid. The pH of the aqueous calcium sulfite slurry 35 can be monitored using any suitable sensor in fluid communication with tank 15. The pH of aqueous solution 35 can also be adjusted or maintained prior to its delivery to tank 15. As will be appreciated by the skilled artisan, the aqueous solution can also comprise a solution or slurry of other sulfite salts.

As will be appreciated, other salts can be oxidized in reactor 10. For example, ferrous iron to ferric iron from mining wastes, can be oxidized in reactor 10. Similarly, any reaction requiring dissolved oxygen are generally applicable.

In some aspects, aqueous solution 35 optionally further includes a surfactant to enhance oxygen transfer to that solution. Surfactants can also be added to aqueous solution 35 to reduce bubble size and/or to reduce foaming of that solution. Suitable surfactants include, for example, sodium silicate or TEFLON® (polytetrafluoroethylene).

Reactor 10 further includes a fine bubble generator that receives an inflow of gas 66. The gas 66 can be any suitable type of oxygen-containing gas, such as air. The fine bubble generator forms a stream of fine bubbles from gas 66 and introduces those bubbles into the aqueous solution 35. As used herein, the term "fine bubbles" means bubbles having a large surface area to volume ratio. The large surface area to volume ratio provides a high rate of oxygen transfer to the aqueous solution 35 in tank 15. Suitable surface area to volume ratios will be from about 5 to about 10, although greater and lesser ratios are within the scope of the invention. Suitable bubble sizes will range from about 0.6 millimeters to about 1.2 millimeters, although greater and lesser sizes are within the scope of the invention. In some embodiments, the gas in the fine bubbles is introduced into the aqueous solution at substantially the same temperature as the ambient air adjacent the tank.

Referring to Figure 1, one example of a fine bubble generator is depicted. The fine bubble generator includes draft tube 55 and rotor 60. As used herein, the term rotor can include a rotor with slots, apertures or teeth in the blades, such as an impeller. Rotor 60 can be driven by, for example, a generally centrally located and vertically oriented rotatable driveshaft 72. Driveshaft 72 is attached to a bearing assembly and drive motor 64. Other suitable mechanisms for driving rotor 60 are also possible and are within the scope of the invention.

The rotor is optionally surrounded by a disperser 63, such as a fenestrated disperser, which is coaxially aligned with the drive shaft 72 and acts to facilitate shearing of gas bubbles and to eliminate excess turbulence within the tank 15. In other embodiments, the fine bubble generator does not include draft tube 55 and/or disperser 63.

As will be appreciated by those skilled in the art, the size of the bubbles created by the fine bubble generator is controlled by a number of factors, including the rotor blade thickness, the rotational speed of the rotor 60, the size and depth of the rotor blades, and optionally, the diameter, area, location of any apertures in a disperser 63 and the thickness of that disperser. Optionally, rotor 60 can have holes or apertures located in the rotor blades to increase the gas bubbles formed by the

fine bubble generator. As rotor 60 rotates, it draws aqueous solution 35 into draft tube 55. The draft tube 55 directs that aqueous solution 35 upwardly towards the rotor 60. The rotation of rotor 60 also draws an oxygen-containing gas 65 into the top of rotor 60. That gas 65 becomes entrained in the aqueous solution 35 by the establishment of a vortex 66. As gas 65 becomes entrained in the liquid, bubbles 69 are formed. Those bubbles 69 are can be further sheared as they pass through disperser 63 to form fine bubbles of oxygen-containing gas.

The position of the fine bubble generator in tank 15 is preferably adjustable, such as by raising or lowering that generator in tank 15 or raising and lowering the liquid level in tank 15. The adjustment of the position of the fine bubble generator with respect to the surface of the aqueous solution 35 facilitates control of the amount of aeration and/or circulation of the aqueous solution 35. For example, if rotor 60 is raised towards the surface of the aqueous solution 35, the amount of aeration is increased. Similarly, if the rotor 60 is positioned deeper in the aqueous solution 35, the amount of aeration is decreased while the amount of pulp circulation is increased.

In some aspects of the invention, the gas 65 can be introduced to rotor 60 through a conduit extending through the driveshaft. In the reactor illustrated in Figure 1, a standpipe or downtube 90 delivers gas 65 to the rotor 60. Gas can also be introduced into reactor 10 by a separate pipe or tube (not shown). The inflow of gas 65 to the fine bubble generator can be assisted by any suitable gas transfer mechanism, such as, for example, a fan, blower, dual load compressor, oil compressor, water compressor or centrifugal-type blow dryer, that injects gas into the upper end of the draft tube 55 or the rotor 60. Referring to Figure 2, reactor 10 includes a blower 80 connected to gas valve 85 by line 83. Blower 80 provides gas pressure equal to about 5-10 feet of water pressure. Other gas transfer mechanisms are possible, according to the depth of rotor 60 and the desired flow of oxygen-containing gas 66.

The rotor 60 further constitutes a mixer to distribute the fine bubbles 69 into the aqueous solution 35 in the tank 15. As those bubbles 69 are distributed into the

aqueous solution 35, they facilitate a high rate of oxygen transfer to that solution. In general, the more thorough the mixing of fine bubbles 69 into aqueous solution 35, the higher the rate of oxygen transfer to that solution. In other embodiments, the mixer can be some other mechanism for distributing bubbles into the aqueous solution 35. For example, the mixer can be a separate rotor, propeller or other mixing device that distributes fine bubbles 69 into the aqueous solution 35. Optionally, the mixer can further include draft tube 55, a disperser 63, and/or a perforated false floor 40 to more uniformly circulate aqueous solution 35.

Referring to Figure 1, the mixer circulates the aqueous solution and distributes the bubbles into the aqueous solution. For example, the mixer can create a circulation path 70 that distributes the bubbles into the aqueous solution and directs the aqueous slurry and bubbles to flow outwardly and towards the walls of the tank 15. In this example, the reduced salt also flows along a circulation path 70. As will be appreciated by the skilled artisan, other circulation paths are possible. In some embodiments, the mixer keeps precipitated salts, such as for example, calcium sulfate, in suspension in the aqueous solution 35. Advantageously, the size of precipitated salt can increase as it flows along a circulation path. The mixer optionally reduces the accumulation of precipitated salts at the surface of the aqueous solution 35, such that the salts are substantially uniformly distributed in the aqueous solution 35. In another embodiment comprising a draft tube and false floor, the aqueous solution 35 flows along the circulation path through perforations in the false floor, into the draft tube, and to the mixer.

Reactor 10 includes a flow diverter to increase the size of the zone of oxidation by directing the flow of fine bubbles and aqueous solution 35 further into tank 15. As will be appreciated by the skilled artisan, the selection and arrangement of flow diverters can control the size and location of the oxidation zone. In some embodiments, the oxidation zone can be 25 percent or more of the volume of aqueous solution 35. Referring to Figure 2, a hood 75 and disperser 63 can increase the size of the oxidation zone by directing the flow of fine bubbles and aqueous solution 35 inwardly and toward the mixer. Referring to Figure 6, a flow diverter

can also constitute baffles 300 disposed about the fine bubble generator. Such baffles 300 extend at least partially between the fine bubble generator and the tank wall(s), or the baffles can fully extend from the fine bubble generator to the tank wall(s). Such baffles 300 are optionally generally vertically disposed. The flow diverter can optionally create a plurality of circulation paths. In other embodiments, either a hood 75, disperser 63 or baffles 300 alone can constitute a flow diverter.

The fine bubble generator is optionally washed and thus kept clean of solids that would otherwise deposit on that generator. Washing also prevents the deposition of solids on the generator that can result from the formation and/or precipitation of the oxidized salt. In the illustrated example in Figure 1, rotor 60 and disperser 63 constitute a washer that directs the flow of aqueous solution 35 over the fine bubble generator. In operation, the washer directs the flow of the aqueous solution over critical surfaces of the fine bubble generator that are subject to solids deposition. That flow prevents the deposition of solids, such as for example, scale, sulfite salts or sulfate salts, on the generator. In another aspect, the washer agitates any precipitated salt so that it remains suspended in the aqueous solution and exerts an abrasive affect on the fine bubble generator, thereby removing any deposited solids from the generator. In other embodiments, the washer can be a rotor or other suitable device.

Referring to Figure 3, another example of the reactor 10 is depicted. The reactor 10 includes a tank 200, rotor 203 and stators 201. The rotor 203 is driven by a vertically to horizontally oriented hollow driveshaft 205. The driveshaft 205 is attached to a bearing assembly and motor 220. Gas 65 passes into an interior cavity of rotor 203 through aperture 209. In some embodiments, the gas can enter the inside of the rotor shaft through gas diffusers 210. In other embodiments, the rotor shaft lacks gas diffusers. The interior cavity preferably is formed at least in part of a gas permeable material, such as for example a perforated material. Aperture 209 can be connected to any suitable gas transfer mechanism, such as, for example, a fan, blower, dual load compressor, oil compressor, water compressor or centrifugal-type blow dryer, that provides a flow of gas 66 into driveshaft 205.

The rotor 203 and stators 201 constitute the fine bubble generator. The rotation of rotor 203 creates a vortex that mixes gas 65 into aqueous solution 35. As gas is injected into that vortex from proximal end 208 of rotor 205, the gas 66 becomes entrained in that solution and bubbles 69 are formed. Those bubbles are further sheared as they pass through stators 201 to form fine bubbles of oxygen-containing gas. The rotor 203 and stators 201 further constitute a mixer to distribute fine bubbles of oxygen-containing gas into the aqueous solution 35. Optionally, a draft tube (not shown) directs the flow of aqueous solution 35 to or from the rotor 203 and stators 201.

The fine bubble generator is optionally washed clean of solids that would otherwise deposit on that generator. The rotor 203 and stators 201 can further constitute the washer that directs the flow of the aqueous solution 35 over critical surfaces of the generator that are subject to solids deposition. That flow prevents deposition of solids, such as for example scale, calcium sulfite and calcium sulfate, on the generator. The washer also agitates any precipitated sulfate salt so that it remains suspended in the aqueous solution and exerts an abrasive affect on the fine bubble generator, thereby removing any deposited solids from the generator.

In another aspect of the invention, a fluid level controller is optionally included in reactor 10. Such a controller monitors the level of the aqueous solution 35 in tank 15. One or more sensing elements detect the level of the surface of the aqueous solution 35 and communicate a signal to a processor. According to the signal(s) from the sensing element(s), the controller can adjust reactor operation. For example, the controller can increase or decrease the amount of aqueous solution entering or exiting the reactor, the speed of the mixer, the amount of aeration, and/or the depth of the fine bubble generator in the aqueous solution. The fluid level controller can also be a foam sensing element in communication with a processing unit. When the foam reaches a defined height above the level of the aqueous solution 35, a signal is generated which can trigger the release of a defoaming agent to reduce the amount of foam.

In a further aspect of the invention, reactor 10 can include a tank 15 with any suitable configuration of fine bubble generators, mixers, washers, and optionally one or more flow diverters. For example, referring to Figure 4, reactor 10 includes a generally rectangular or circular tank 15, or a trench (not shown). Three rotors 60 are driven by motor 64. Each rotor 60 is optionally surrounded by a coaxially extending diffuser 63 or other flow diverter. Draft tube 55 receives and directs the flow of aqueous solution 35 to the fine bubble generator. Standpipes 90 receive oxygen-containing gas 66 from gas transfer mechanism 80 through line 112. A reduced salt, such as an aqueous solution or slurry, enters tank 15 through inlet 25 and oxidized salt is withdrawn through outlet 30. Other configurations of reactor 10 are possible, as will be appreciated by those skilled in the art.

In still another aspect, an oxidative reactor system facilitates the oxidation of one or more reduced salts to their oxidized form(s). One or more oxidative reactors can be connected in series and/or in parallel. This arrangement allows individual reactors to be taken off-line for maintenance and/or repair without the need to empty the system during such maintenance or repair. The system further provides a method for continuous processing of salts.

Referring to Figures 5a and 5b, examples of continuous processing systems are depicted. Figure 5a depicts reactors 10 connected in series for serial processing of reduced salts. Reactors 10 are interconnected by lines 102, which provide fluid communication between those units. Line 101 connects the first reactor to any suitable source 100 of reduced, such as a slurry or solution containing reduced salt. Such a source can include a flue gas desulfurization scrubber or other pollution control equipment that produces reduced salt (*e.g.*, sulfite) in any form, including wet and dry forms. Other suitable sources of reduced salts will include storage ponds, landfills, mine leachates and the like. Each reactor 10 holds a quantity of aqueous reduced salt. As the aqueous salt moves from reactor to reactor, the amount of oxidized salt in the aqueous solution increases. As will be appreciated by those of skill in the art, by regulating the delivery of oxygen-containing gas in each reactor, the oxygenation of the aqueous solution, and the residence time of that



solution in each reactor, the efficiency of the oxidation process can be controlled. Line 108 connects the last reactor 10 to another component 110, such as, for example, a dewatering device, dryer or storage tank. Suitable dewatering devices can include, for example, a hydrocyclone or horizontal belt vacuum filter. Multiple dewatering devices can be connected in series and/or parallel. For example, the hydrocyclone can be used in a first stage of a dewatering process followed by drying on a filter. Optionally, a gas transfer mechanism (not shown) is in fluid communication with one or more reactors 10 to provide higher rates of gas delivery to reactors 10.

Figure 5a also depicts an example of flow lines and valves which allow control the flow of aqueous solution to and from individual reactors 10. Flow lines 105 and valves 106 provide a pathway for diverting the flow of aqueous solution 35 to or from one or more reactors 10. For example, in some instances it can be desirable to bypass individual reactors for maintenance or repair. Similarly, additional reactors can be brought on-line to spare other reactors, to increase the efficiency of the oxidation process or to handle materials that have lower oxidation rates.

Referring to Figure 5b, a parallel processing system is depicted. A suitable source 100 of salt 100, such as, for example, a flue gas desulfurization scrubber or other pollution control equipment, is in fluid communication with reactors 10 through lines 101. Other suitable sources of reduced salts will include storage ponds and/or landfills. Valves 106 control the flow the aqueous solution to each reactor 10. Lines 108 provide for the discharge of sulfate from reactors 10. Lines 108 are in fluid communication with another component 110, which can include a dewatering device or storage tank. As depicted in this example, a gas transfer mechanism 80 is in fluid communication with one or more reactors 10 through lines 112 to provide higher rates of gas delivery to reactors 10. As will be appreciated by those skilled in the art, the system is not limited to the examples illustrated in these Figures 5a and 5b.

In another aspect of the invention, a method for oxidizing salts is provided. A reduced salt, such as for example calcium sulfite, is introduced into tank 15 of reactor 10. Such calcium sulfite is preferably an aqueous slurry of calcium sulfite within the range of about 5% to about 25% (w/v) suspended solids, although greater and lesser amounts are within the scope of the present invention. Other reduced salts, such as sodium, magnesium and/or ammonium salts or iron sulfate, can be introduced into tank 15 in any suitable concentrations, as will be appreciated by those skilled in the art. The reduced salt can optionally be delivered from an external storage vessel, from a scrubbing unit, such as for example, a magnesium-enhanced lime scrubber, a non-magnesium-enhanced scrubber or a limestone-based scrubber, or from another source of reduced salt, such as a storage pond, landfill or mine. If necessary, the pH of the aqueous solution 35 is adjusted to facilitate oxidation and/or precipitation of the sulfite to its sulfate form. For example, for calcium sulfite slurries, the pH can be adjusted to within the range of about pH 3 to 7, more preferably to between about 4.5 to about 5.5. The pH of the aqueous solution 35 can be adjusted in the tank 15 by the addition of a suitable acid, such as, for example, sulfuric acid, or any suitable base. For some processing operations, it can be preferable to adjust the pH of aqueous solution 35 prior to its introduction into tank 15.

In operation, a flow of fine bubbles of an oxygen-containing gas is delivered to the aqueous solution in the tank 15. For example, referring to Figure 1, as rotor 60 rotates it also draws oxygen-containing gas 65 into standpipe 90 and aqueous solution 35 into the lower end of the rotor 60. Gas 66 becomes entrained into the aqueous solution 35 by the establishment of a vortex. As gas 66 is entrained in the aqueous solution 35, bubbles 69 are formed. Those bubbles 69 can be further sheared by the rotation of rotor 60 and, optionally, the flow of aerated aqueous solution 35 through disperser 63. Referring to Figure 3, rotor 203 and stators 201 can also form and deliver a flow of fine bubbles to the aqueous solution. For example, the rotation of rotor 203 creates a vortex that mixes gas 65 into aqueous solution 35. As gas is injected into that vortex from proximal end 208 of rotor 203,

the gas 65 becomes entrained in that solution and bubbles 69 are formed. Those bubbles are further sheared as they pass through stators 201 to form fine bubbles of oxygen-containing gas.

The bubbles 65 facilitate oxygen transfer to the reduced salt in solution 35. As the oxygen dissolves in that solution, it reacts with the salt and oxidizes its. For some oxidation processes, the oxidized salt can precipitate as it forms. For example, calcium sulfate can precipitate as it forms if the solution has reached its saturation point. Precipitation can be assisted by the presence of small particles or crystals in the aqueous solution 35. If the reduced salt in solution is in equilibrium with suspended solids, the solids will dissolve as the oxidized salt precipitates. In other oxidation processes, the reduced and oxidized salts are both dissolved in solution 35.

In batch operations, substantially all of the reduced can be oxidized before the oxidized salt is discharged from the reactor. In a continuous processing mode, the conversion efficiency can be controlled by the surface area to volume ratio of the fine bubbles, the amount of oxygen introduced, the efficiency of oxygen transfer to the aqueous solution, the resulting partial pressure of oxygen in that solution, and the residence time in the reactor 10.

The oxidation of reduced salt to its oxidized form can be enhanced by mixing the fine bubbles of oxygen-containing gas with the aqueous solution 35. Such mixing can provide a high rate of oxygen transfer to the aqueous sulfite solution 35. For example, in Figure 1 the rotor 60 and disperser 63 create a circulation path 70 that distributes the bubbles throughout the aqueous solution 35 in tank 15.

The fine bubble generator is optionally cleaned to prevent the deposition of solids on, and to aid in removal of such solids from, that generator. For example, cleaning can be effected by the circulation path 70 of aqueous solution 35. Cleaning occurs as aqueous solution 35, and optionally any precipitated salt, flow over the critical surfaces of the fine bubble generator. That flow prevents the deposition of solids on the generator. More particularly, any crystalline salt can

provide abrasion at the critical surfaces of the fine bubble generator to remove any solids deposited, or tending to deposit, on that generator.

Following the conversion of the reduced salt to its oxidized form, the oxidized salt is withdrawn from reactor 10. In one aspect of the invention, the oxidized salt is then precipitated. In another aspect of the invention, the oxidized salt is dewatered, such as for example in a hydrocyclone, although other methods of dewatering are within the scope of the invention. The oxidized salt can be further dried on a filter, such as, for example, a horizontal belt vacuum filter. Alternatively, the oxidized salt is transferred to manufacturing or storage facilities for subsequent use or disposal. The method can also be suitably performed in accordance with other aspects of the reactors and/or systems, as described herein.

Other embodiments of the present invention are exemplified in the following examples. These examples illustrate working principles of the present invention, although the present invention is not intended to be limited by or to these examples.

*Example 1:*

Sulfur dioxide is scrubbed from the discharge of a thermal power plant using magnesium-enhanced lime, non-magnesium enhanced lime, or limestone-air scrubbers. The flue gas desulfurization process creates calcium sulfite, which is fed into an oxidative reactor system. The calcium sulfite is 0-60% oxidized before it enters the system. In the reactor, the aqueous slurry of calcium sulfite has a pH of about 5.5. The oxidative reactor uses air as the source of the oxygen-containing gas to generate fine bubbles within the range of about 0.6 to about 1.2 millimeters. Those bubbles are introduced into the aqueous calcium sulfite slurry to oxidize the sulfite to form a calcium sulfate slurry. After a residence time of between about 2-6 hours, greater than 99% of the calcium sulfite is oxidized to calcium sulfate.

*Example 2:*

The blowdown from a flue gas desulfurization scrubber is fed to a series of oxidative reactors using blown air as the source of the oxygen-containing gas. The

oxidation of the calcium sulfite take place in the scrubber and in the reactor. Greater than 99% of the calcium sulfite is oxidized.

*Example 3:*

A 3.5 liter reactor contains either 16% or 26% suspended calcium sulfite solids. Air is used as the source of the oxygen-containing gas to generate fine bubbles within the range of about 0.6 to about 1.2 millimeters. Oxygen (in the air) is delivered to the aqueous calcium sulfite slurry at a rate of about 2 liters per minute, or about 28.5 g per hour. Oxygen is utilized to oxidize calcium sulfite to calcium sulfate at a rate of about 23.8 g per hour, for an efficiency of 83%.

*Example 4:*

A 3.5 liter reactor contains 180 g/l dissolved ammonium sulfite. Air is used as the source of the oxygen-containing gas to generate fine bubbles within the range of about 0.6 to about 1.2 millimeters to produce ammonium sulfate. Ammonium sulfite is reacted at a rate of 0.51 g/l/minute.

*Example 5:*

A 3.5 liter reactor contains 46 g/l dissolved magnesium sulfite. Air is used as the source of the oxygen-containing gas to generate fine bubbles within the range of about 0.6 to about 1.2 millimeters to produce magnesium sulfate. Magnesium sulfite is reacted at a rate of 1.35 g/l/minute.

*Example 6:*

Calcium sulfite, such as from a land fill or pond, is slurried with water or with scrubber blowdown material in a mix tank. The resulting slurry is fed to an oxidative reactor. The oxidation of calcium sulfite to calcium sulfate takes place in the reactor, where greater than 99% of the calcium sulfite is oxidized to calcium sulfate.

*Example 7:*

An aqueous solution of magnesium, ammonium, and/or sodium sulfite is introduced to an oxidative reactor, which has a fine bubble generator and a mixer. A flow diverter comprising baffles directs the flow of aqueous solution inwardly and towards the mixer, so as to form a circulation path. As the oxygen from the fine bubbles reacts with the sulfite salt, sulfate salts are formed. After the oxidation reaction is substantially complete, the aqueous solution is withdrawn from the reactor, and the sulfate salts are precipitated from that solution

Having thus described in detail the preferred embodiments of the present invention, it is to be understood that the invention defined by the appended claims is not to be limited by particular details set forth in the above description, as many apparent variations thereof are possible without departing from the spirit or scope thereof.

## CLAIMS

We claim:

1. An oxidative reactor to support the formation and precipitation of calcium sulfate from calcium sulfite, said reactor comprising:
  - a tank, having walls and a bottom, for holding an aqueous slurry of calcium sulfite;
  - an inlet in said tank for delivery of said aqueous slurry from a source thereof to said tank;
  - a fine bubble generator in fluid communication with said aqueous slurry for introducing fine bubbles of an oxygen-containing gas into said aqueous slurry;
  - a flow diverter within said tank to reduce rotation of said aqueous solution in said tank; and
  - a mixer in said tank to distribute said bubbles into said aqueous slurry and to maintain the circulation of said aqueous slurry and bubbles in said tank;whereby a circulation path for said aqueous slurry and bubbles is created in said tank defining an oxidation zone occupying a significant volume of the tank, and said precipitated calcium sulfate circulates in said circulation path.
2. The reactor according to claim 1,
  - wherein said gas is air.
3. The reactor according to claim 2,
  - wherein said air in said fine bubbles is introduced into the slurry at substantially the same temperature as the ambient air temperature adjacent said tank.
4. The reactor according to claim 1, further comprising:
  - a rotor rotatable in said tank and constituting at least part of said fine bubble generator and said washer.
5. The reactor according to claim 4,

wherein said rotor constitutes said mixer.

6. The reactor according to claim 4,  
wherein said rotor has an interior cavity, is formed at least in part of gas permeable material defining said cavity, receives gas under pressure at said cavity, and constitutes at least part of said fine bubble generator.
7. The reactor according to claim 4, further comprising:  
a stator assembly around said rotor defining flow paths for said aqueous slurry and constituting at least part of said mixer.
8. The reactor according to claim 1, further comprising:  
a standpipe mounted above said fine bubble generator for delivering said oxygen-containing gas to said fine bubble generator.
9. The reactor according to claim 1, further comprising:  
a washer for cleaning said fine bubble generator of solids that result from the formation and precipitation of said calcium sulfate.
10. The reactor according to claim 9, further comprising:  
a draft tube mounted below said mixer for directing the flow of said aqueous slurry to said fine bubble generator and said mixer, said draft tube constituting at least part of said flow diverter.
11. The reactor according to claim 10, further comprising:  
a false floor positioned below said draft tube;  
whereby said draft tube and false floor together constitute at least part of said flow diverter.
12. The reactor according to claim 1, further comprising:  
an outlet in said tank for discharge of sulfate compounds from said tank, said inlet and said outlet positioned at spaced locations around said tank, but at substantially the same elevation from said tank bottom.
13. The reactor according to claim 1,  
wherein said tank has a top at least partially vented to the atmosphere, whereby the reaction of oxygen and sulfite compounds to form sulfate compounds is an exothermic reaction generating heat and said partially open



top releases said gas and heat from said reactor to the atmosphere and facilitates adiabatic cooling of said aqueous slurry.

14. The reactor according to claim 1,  
whereby the size of said precipitated sulfate compounds increases as said precipitate flows along said circulation path.
15. An oxidative reactor system for oxidizing salts in an aqueous solution, said system comprising:
  - at least one tank, having walls and a bottom, for holding said aqueous solution of a reduced salt;
  - at least one inlet in said tank for delivery of said solution from a source thereof to said tank;
  - at least one fine bubble generator in fluid communication with said solution for introducing fine bubbles of an oxygen-containing gas into said solution; and
  - at least one flow diverter within said tank to reduce rotation of said aqueous solution in said tank; and
  - at least one mixer in said tank to distribute said bubbles into said aqueous slurry and to maintain the circulation of said aqueous solution and bubbles in said tank;whereby at least one circulation path for said aqueous solution and bubbles is created in said tank defining an oxidation zone occupying a significant volume of said tank, and said oxidized salts flow along said at least one circulation path.
16. The system according to claim 15, further comprising:
  - at least one scrubber constituting said source of said aqueous solution.
17. The system according to claim 15, further comprising:
  - at least one washer for cleaning said fine bubble generator of solids that result from the formation of said oxidized salt.
18. The system according to claim 15,  
wherein said gas in said fine bubbles is introduced into said aqueous

solution at substantially the same temperature as the ambient air temperature adjacent said at least one tank.

19. The system according to claim 15,  
wherein said aqueous solution is an aqueous slurry of calcium sulfite.
20. The system according to claim 15, further comprising:  
at least one dewatering device for removing water from said sulfate salt discharged from said tank.
21. The system according to claim 20,  
wherein said at least one dewatering device is a hydrocyclone.
22. The system according to claim 20, further comprising:  
a second dewatering device downstream of said at least one dewatering device.
23. The system according to claim 22,  
wherein said second dewatering device comprises a vacuum filter.
24. A method for formation of oxidized salts from an aqueous solution of salts, comprising:  
providing a tank having an inlet;  
introducing an aqueous solution containing a reduced salt to said tank;  
delivering a flow of fine bubbles of an oxygen-containing gas to said tank via a fine bubble generator;  
mixing said bubbles and said solution to distribute said bubbles into said aqueous solution to provide a high rate of oxygen transfer to said aqueous solution;  
reducing the rotation of the aqueous solution in said tank; and  
oxidizing said salt to its oxidized form; and  
circulating said aqueous solution and said bubbles in said tank,  
whereby said oxidized salt is substantially uniformly distributed in said aqueous solution.
25. The method according to claim 24,  
providing air as said gas.

26. The method according to claim 24,  
providing said gas at substantially the same temperature as the  
ambient air temperature adjacent said tank.
27. The method according to claim 24, further comprising:  
adjusting the pH of said aqueous solution to between about 3 and  
about 7.
28. The method according to claim 24, further comprising:  
providing said aqueous solution from a scrubber.
29. The method according to claim 28, further comprising:  
desulfurizing flue gas in said scrubber to form a reduced salt  
comprising a sulfite.
30. The method according to claim 24, further comprising:  
cleaning said bubble generator of solids tending to accumulate on said  
generator.
31. The method according to claim 24, further comprising:  
dewatering said oxidized salt.

1/4

FIG. 1

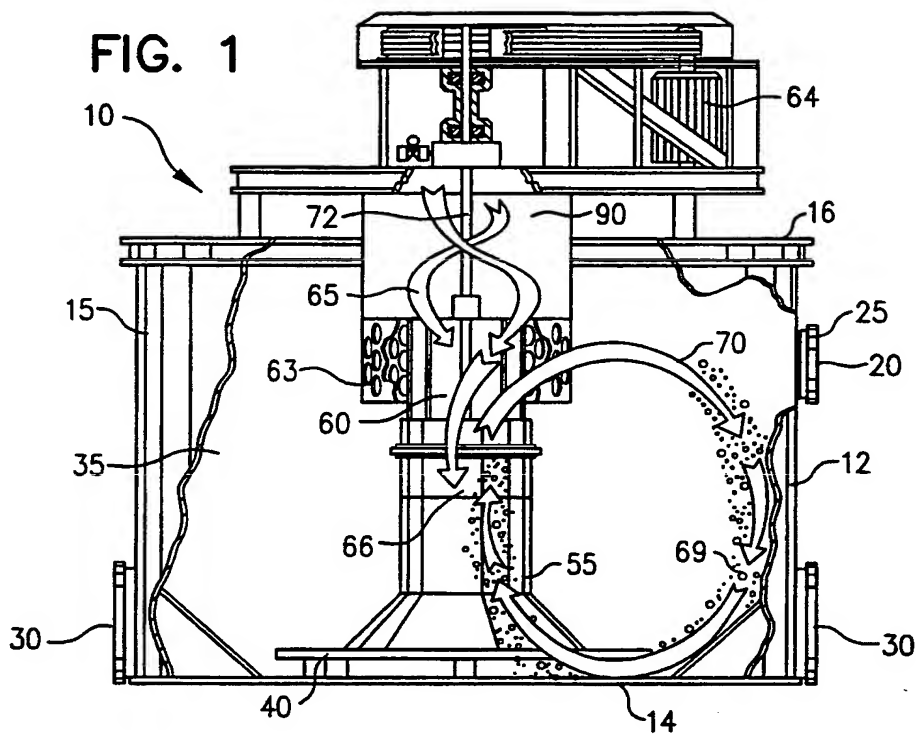
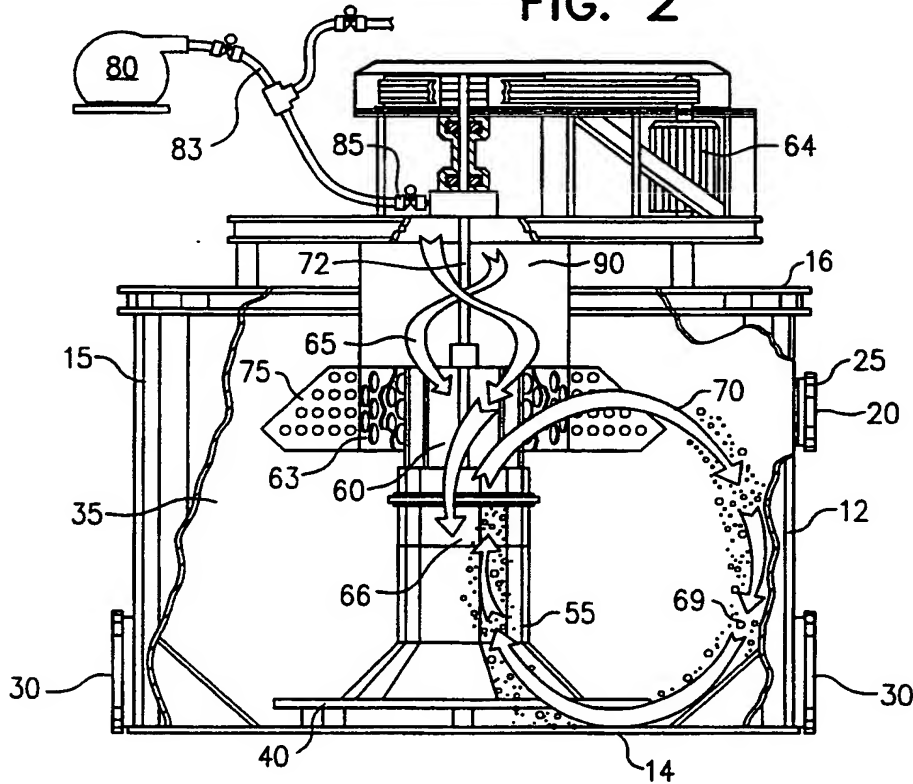


FIG. 2



2/4

FIG. 3

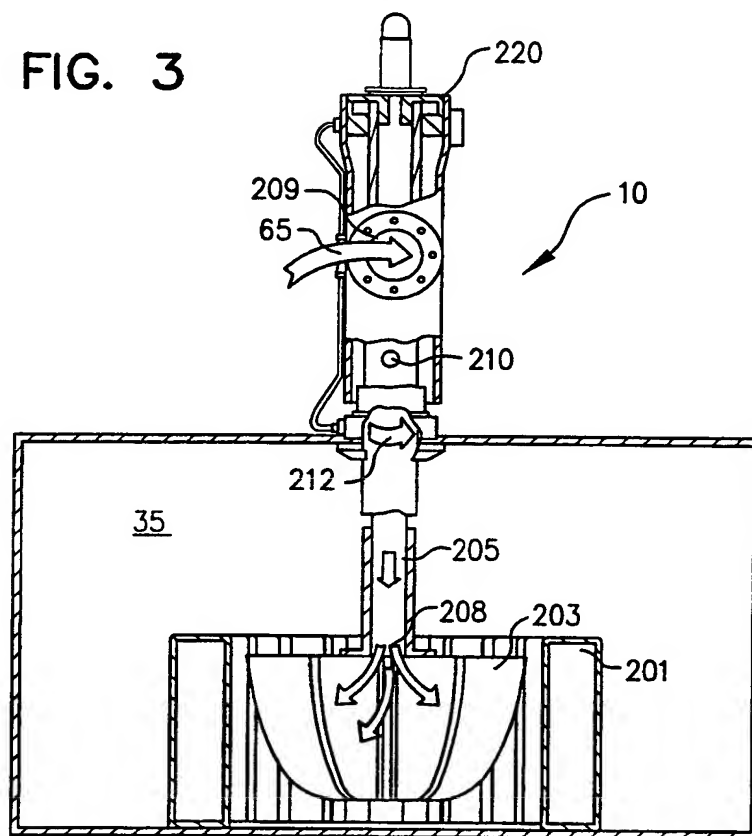
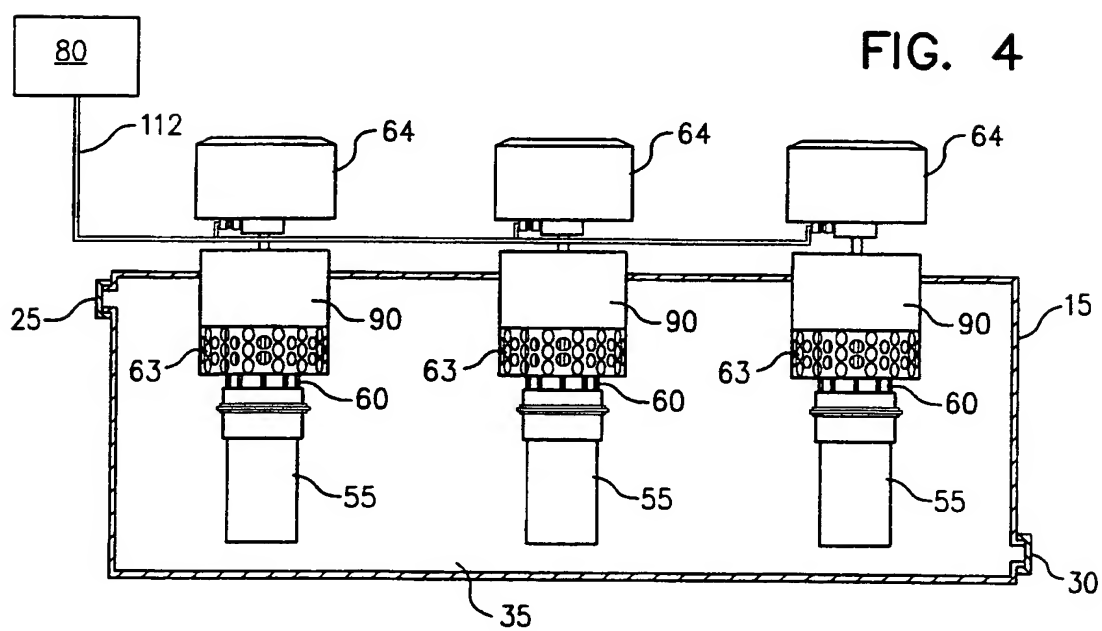


FIG. 4



3/4

FIG. 5A

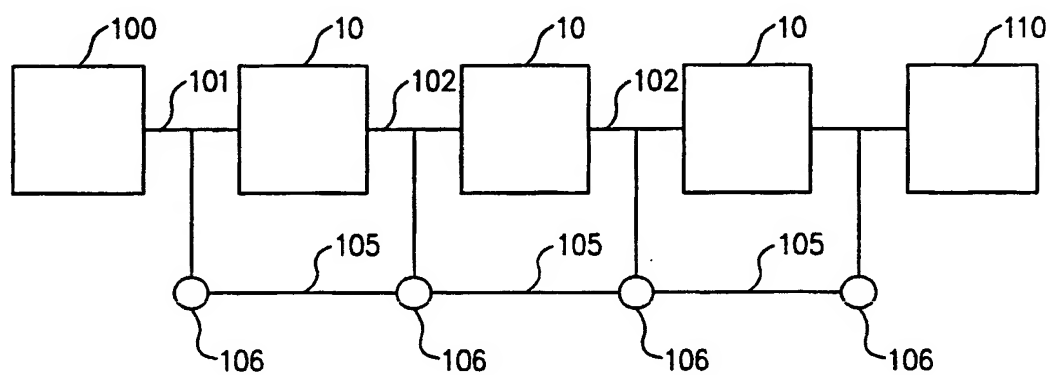
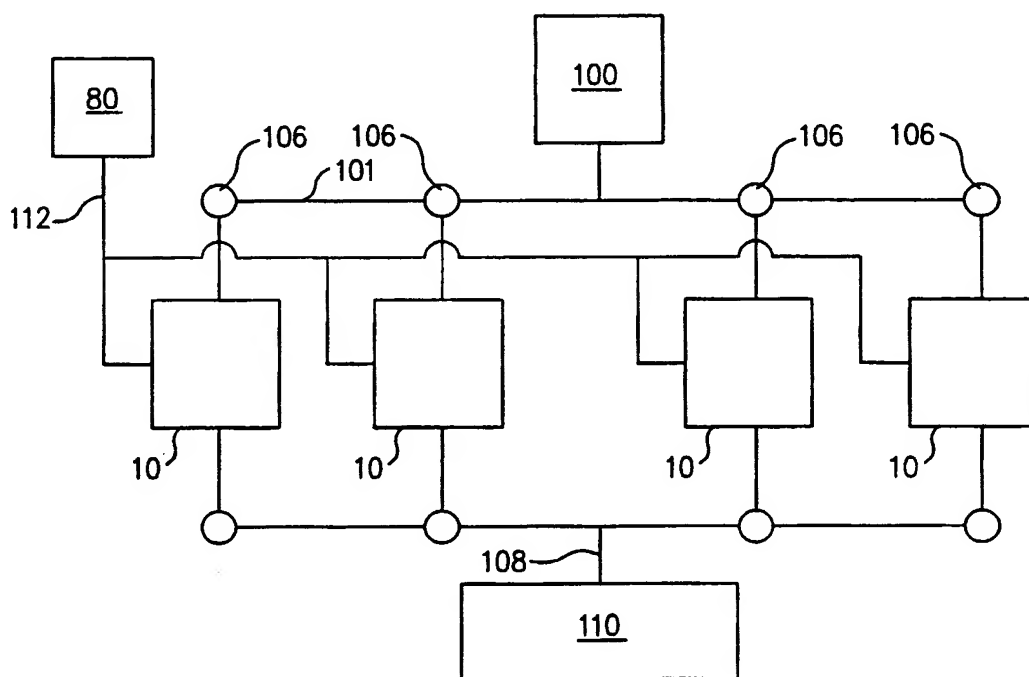


FIG 5B



4/4

FIG. 6

